AD715776

The Thermal Stability of Nitrilotriacetic Acid and Its Salts in Aqueous Solutions

DAVID L. VENEZKY

Inorganic Chemistry Branch

and

WILLIAM B. MONIZ

Physical Chemistry Branch
Chemistry Division

November 17, 1970

NAVAL RESEARCH LABORATORY
Washington, D.C.

·13

ABSTRACT

A proposed mechanism for the thermal decomposition of ethylenedinitrilo-tetraacetic acid (H_4EDTA) and its salts suggests an intermediate having a hydrogen three-centered bridge structure. To elucidate the mechanism of $EDTA^{4-}$ decomposition and to establish structures which would impart inherent thermal stability to a chelating compound, nuclear magnetic resonance (nmr) techniques were used to study the thermal stability of nitrilotriacetic acid (H_3NTA) and its salts. These compounds have a structure similar to $EDTA^{4-}$ but are not capable of forming a three-center intramolecular bridge under any circumstance.

Degassed and undegassed aqueous solutions of Na_3NTA, and Na_2HNTA and a degassed solution of H_3NTA were heated at 200°C in sealed nmr tubes for periods ranging from 1 hr to over 670 hr. Periodic examination of the contents using proton magnetic resonance (pmr) showed that dissolved oxygen has little effect on the decomposition of Na_3NTA and Na_2HNTA solutions. For one-half of the initial concentrations to decompose at 200°C, the estimated times for both degassed and undegassed solutions of Na_3NTA and Na_2HNTA were greater than 1000 hr. The estimated $t_{1/2}$ for H_3NTA solutions is 12 hr, for H_4EDTA solutions, 1 hr, and for Li_4EDTA solutions, the most stable $EDTA^{4-}$ solutions studied so far by the nmr techniques, 13 hr. Although the laboratory results show that NTA^{3-} is far more stable than $EDTA^{4-}$ at 200°C, it would be unsafe to predict that NTA^{3-} would continue to show this excellent thermal stability up to 300 through 320°C. A different mode of thermal decomposition, not dependent on the proposed protonation of NTA^{3-}, may occur readily at temperatures higher than 200°C. In basic solutions at 200°C and lower, the uncomplexed or weakly complexed NTA^{3-} should be stable enough to be useful as a boiler-water additive for sludge control and feed-water conditioning. Under the restrictive conditions, water contamination from thermally decomposed NTA^{3-} should be minimal and should occur only after prolonged heating.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

THE THERMAL STABILITY OF NITRILOTRIACETIC ACID
## AND ITS SALTS IN AQUEOUS SOLUTIONS

INTRODUCTION

A perusal of the literature (1) indicates a substantial increase in the use of organic chelating agents for treatment of boiler feed water. Two chelating agents, ethylenedinitrilo-tetraacetic acid (H_4EDTA) and nitrilotriacetic acid (H_3NTA) in the form of their sodium salts, have been studied extensively for use in cleaning boilers and in treating the boiler feed water. Organic chelating agents in boiler feed water reduce sludge formation by forming soluble complexes with calcium, magnesium, and iron, the major cations found in the undesirable insoluble deposits. Boilers which have been operated for many years with either $EDTA^{4-}$ or NTA^{3-} have shown excellent resistance to blowouts, deposit formation, and pitting within the boiler. Furthermore, if an excess of a chelating agent is added to the boiler feed water, previously formed deposits would be removed by the free or uncombined chelating agent. Unfortunately, little work has been reported on the thermal stability of these organic chelating agents in aqueous solutions at high temperatures to determine if the excess organic reagent would have a long enough existence to be beneficial.

A recent NRL investigation of the thermal decomposition of H_4EDTA and several of its salts in aqueous solutions indicated that the decomposition is accelerated as the pH of the solution is lowered (2). One proposed mechanism of the observed decomposition at 200°C is the association of a proton with the $EDTA^{4-}$ structure, which then facilitates the splitting of a "CH_2CO_2" group from the structure in a stepwise fashion:

$$
\begin{array}{l}
^-OCCH_2 \quad\quad H \quad\quad CH_2CO^- \\
\;\;\Vert \quad\quad\quad / \;\; \\
\;\;O \quad NCH_2CH_2N \quad O \\
\quad\quad / \quad\quad\quad\quad \backslash \\
^-OCCH_2 \quad\quad\quad CH_2CO^- \\
\;\;\Vert \quad\quad\quad\quad\quad \Vert \\
\;\;O \quad\quad\quad\quad\quad O
\end{array}
\longrightarrow
\begin{array}{l}
^-OCCH_2 \quad\quad\quad H \\
\;\;\Vert \quad\quad\quad\quad / \\
\;\;O \quad NCH_2CH_2N \\
\quad / \quad\quad\quad\quad \backslash \\
^-OCCH_2 \quad\quad CH_2CO^- \\
\;\;\Vert \quad\quad\quad\quad \Vert \\
\;\;O \quad\quad\quad\quad O
\end{array}
+ CO_2 + ?
$$
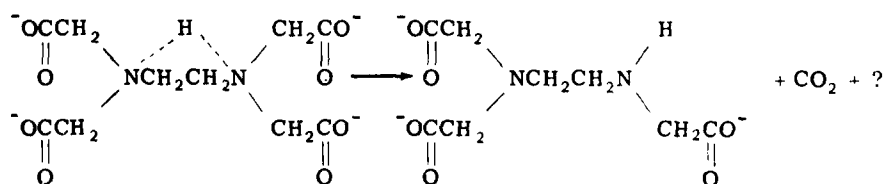
In the presence of protons, the process can continue until all of the $EDTA^{4-}$ has been decomposed into small fragments. Such fragments, which may not have the desired chelating properties of the original material, may actually have deleterious effects within the boiler or may affect the pH control of the boiler water.

Because of the need for thermally stable materials of good chelating properties, the proposed mechanism of decomposition through an intermediate having a hydrogen three-centered bridge structure, such as described by Fujiwara and Reilley (3), suggests two points which should be examined to elucidate the mechanism of decomposition and to establish structures which would impart inherent thermal stability to a chelating compound: (a) the effect of preventing hydrogen-bridge formation in $EDTA^{4-}$ by complexing the nitrogens in $EDTA^{4-}$ with a strong Lewis acid, and (b) the thermal stability of materials whose structure

$$N(-CH_2 \overset{\overset{\displaystyle O}{\Vert}}{C} -O)_3{}^{3-}$$

1
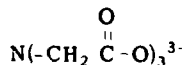
is similar to EDTA^{4-} but is not capable of forming a three-center intramolecular bridge under any circumstance. The first factor will be examined in a future report (4). This report discusses the thermal stability of the chelating agent H_3NTA and its sodium salts in aqueous solutions heated to 200°C. The structure of NTA^{3-} does not allow the formation of the postulated bridge structure but will allow the study of the effect of protonation when only one nitrogen is available per molecule of chelating agent.

EXPERIMENTAL PROCEDURE

The nmr technique used has been reported previously (2). The sealed nmr tubes were monitored, after heating at 200°C ± 5° and cooling, by running the spectra on a Varian HA/100 in the frequency sweep mode. The sample temperature in the spectrometer was maintained at 24°C, and the water peak was used as the locking signal. Peak positions are given in hertz upfield from the water peak, and initial sample peak heights have been normalized to 100%.

Trisodium nitrilotriacetate (technical grade), disodium nitrilotriacetate (practical grade), and nitrilotriacetic acid (reagent grade) from the J. T. Baker Chemical Company were used without further purification. Demineralized, distilled water was used to prepare the solutions.

The solutions of the sodium salts were prepared as stock solutions: Na_3NTA, 0.20M, pH = 9.88 and Na_2HNTA, 0.20M, pH = 8.34. Sufficient acid, which was not completely soluble in water, was weighed in an nmr tube to make 0.5 ml of a hypothetical 0.30M solution; the pH of this saturated solution at room temperature was 1.98. The effect of oxygen on the rate of decomposition was studied by comparing degassed solutions of Na_3NTA and Na_2HNTA with undegassed solutions. The degassed solutions were sealed after four freeze-thaw cycles under reduced pressure (10^{-4} to 10^{-5} torr). Undegassed solutions were sealed under reduced pressure immediately after freezing the solutions at liquid nitrogen temperature.

The sealed nmr tubes in a protective iron jacket were heated in an oven set at 200°C ± 5°. The nmr spectrum of a sample was determined before and after each period of heating.

RESULTS AND DISCUSSION

For NTA^{3-} the single pmr peak attributed to the methylenic protons can be conveniently used to follow the rate of thermal decomposition of NTA^{3-} in aqueous solutions. The Na_2HNTA solutions (pH = 8.34) exhibited the expected single peak initially at 107 Hz (Fig. 1). The pmr spectra for Na_3NTA solutions (pH = 9.98) consist of a strong sharp resonance at 150 Hz and a weak peak at 83 Hz (Fig. 2). The latter peak is attributed to an impurity in the technical-grade reagent used. The impurity present may be a strong Lewis acid, which would cause a peak downfield from the uncomplexed peak (150 Hz) similar to the shift noted for Mo(VI)-NTA complexes (5). Because the peaks attributed to uncomplexed NTA^{3-} showed little effect after heating the Na_3NTA and Na_2H^{-}TA solutions at 200°C for up to 672 hours, the traces of impurities which may have been present were not considered to be detrimental to the observed results.

Unlike the sodium and lithium salts of EDTA^{4-} (2), the sodium salts of NTA^{3-} showed a remarkable stability in aqueous solutions heated at 200°C. A comparison of the times for one-half of the sample to decompose is shown in Table 1. The proton peak heights for both the degassed and undegassed solutions of Na_3NTA (Fig. 3) remained at 100 ± 5% for 106 hours. A 12% reduction in peak height of the degassed sample was noted after

Fig. 1 - Nmr spectra of a degassed 0.20M solution of Na_2HNTA sealed under reduced pressure and heated to 200 °C
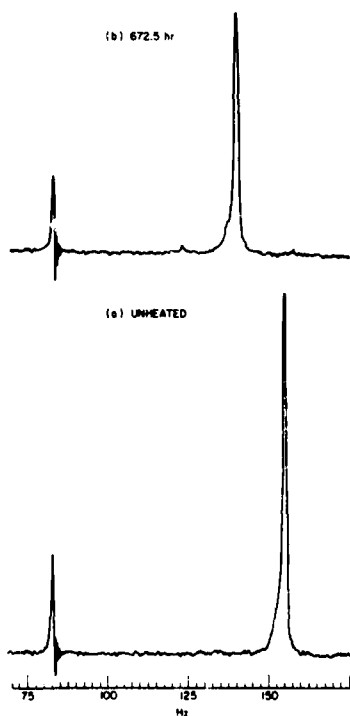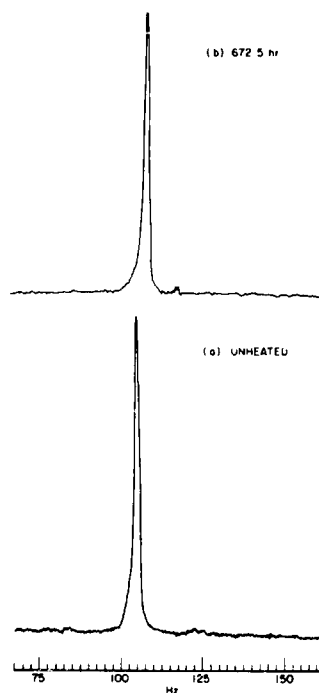

Fig. 2 - Nmr spectra of a degassed 0.20M solution of Na_3NTA sealed under reduced pressure and heated to 200 °C

Table 1
Estimated Times for One-Half of the Initial Concentrations of EDTA^{4-} and NTA^{3-} Aqueous Solutions to Decompose at 200°C

Salt	Initial Solution Concentration (M)	Initial pH	$t_{1/2}$ (hr)
Na$_2$H$_2$EDTA	0.25	4.5	3
Li$_4$EDTA	0.13	9.8	13
H$_4$EDTA	0.24*	2.8†	1
Na$_2$HNTA	0.20	8.3	>1000
Na$_3$NTA	0.20	9.9	>1000
H$_3$NTA	0.30*	2.0†	12

*Saturated solution plus enough solid acid to give the indicated concentration.
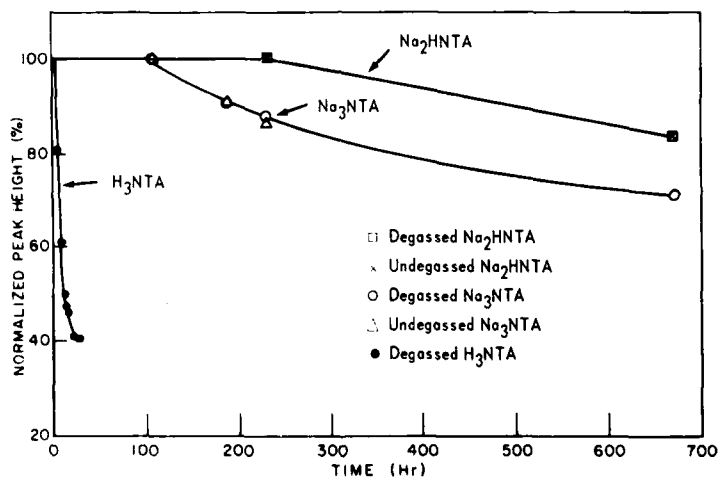†pH of the saturated solution at room temperature.

Fig. 3 - Change in normalized peak height with respect to length of heating sealed solutions under reduced pressure. The solutions were heated to 200°C.

232 hours at 200°C and after 672 hours the peak had been reduced 29%. After 236 hours, the proton peak height of the Na$_3$NTA solution was reduced 14%, but the sample tube shattered during the 440-hour final heating.

The Na$_2$HNTA solutions (Fig. 3) appeared to be even more stable than the Na$_3$NTA solutions. After 232 hours at 200°C, no significant difference was noted between the degassed and undegassed solutions; both remained at 100 ± 5% of initial peak height. After 672 hours, the peak heights had decreased 17% of their original value.

The position of the proton peak in the pmr of the Na_2HNTA solutions remained rela-
tively constant, 108.0 Hz ($\cdot$ = ±0.5 Hz), throughout the 672 hours of heating at 200°C
(Fig. 1). The initial proton resonance at 154.8 to 155.0 Hz observed for the Na_3NTA
solutions (Fig. 2) shifted to approximately 152 Hz after the first hour of heating and then
remained nearly constant at 151.7 Hz ($\cdot$ = ±0.6 Hz) and 151.4 Hz ($\cdot$ = ±0.6 Hz) for the
undegassed and degassed solutions, respectively. After 672 hours, the peak in the degassed
sample had shifted downfield to 139.6 Hz. The peak in the undegassed sample had shifted
downfield to 148.2 Hz at 232 hours.

Chan, Kula, and Sawyer (5) observed the variation with pH of methylene proton chemical
shifts of NTA^{3-} solutions. The reported curve consisted of three plateau regions: below
pH = 0, between approximately pH = 4 and 8, and above pH = 11. The downfield shift
between approximately pH = 11 and 8 was attributed to the protonation of the nitrogen atom.
The 15-Hz downfield shift observed here for heated Na_3NTA solutions, initial pH = 9.9,
is consistent with a decrease in pH of the solution. Because the pH of the Na_2HNTA solu-
tion falls in the plateau region around pH = 8, the effect of heating on solution pH is
indeterminate. Based on the conclusions of Chan et al. that the 50-Hz upfield shift between
pH = 0 and 4 is attributable to successive deprotonation of the carboxylate groups, the
upfield chemical shift of 24 Hz observed for the heated H_3NTA solution (initial pH = 2.0) is
consistent with an increase in pH as the acid decomposes.

To compare the apparent rates of decomposition, the normalized peak heights (100% =
initial value) are plotted as a function of time in Fig. 3. The Na_2HNTA solutions show a
longer period over which no decomposition is detected than do the Na_3NTA solutions.
Although dissolved oxygen had no effect on the decomposition rate of the Na_2HNTA solu-
tions, the undegassed Na_3NTA solution showed a slightly greater rate of decomposition
than did the corresponding degassed solution. The deleterious effect of dissolved oxygen
on the Na_3NTA sample may be indicated by the rupturing, during the final 440-hour
heating period, of the nmr tube containing the solution that was not degassed. However,
solutions of the sodium salts of NTA^{3-}, degassed or undegassed, were orders of magnitude
more stable than degassed Na_2H_2EDTA and Li_4EDTA solutions. Detectable decomposition
of the $EDTA^{4-}$ was usually noted after the first hour or two of heating at 200°C, and
complete decomposition was detected after 10 to 20 hours for Na_2H_2EDTA solutions and
after 130 to 200 hours for Li_4EDTA solutions (2).

Similar to H_4EDTA, H_3NTA is slightly soluble in water but not sufficiently soluble
at room temperature to be detected by pmr. However, after the first hour of heating, the
solution of H_3NTA was clear when the sample was first placed in the nmr probe. Unfor-
tunately, a solid precipitated from the supersaturated solution, causing the pmr signals
to shift and vary in intensity (pH and concentration effects, respectively). Two peaks,
at 71.8 Hz and 88.6 Hz, were recorded (Fig. 4a). After 3 hours total heating, a relatively
strong peak (maximum intensity for this solution) was observed at 69.6 Hz with a weak
peak at 88.1 Hz (Fig. 4b). Solid still precipitated from the solution during the pmr run.
A yellow-brown solution, with little solid, formed in the tube after 6 hours total heating.
A new feature, a triplet centered at 210 Hz(Fig. 5b), was now quite prominent in the pmr
spectrum and the intensity of the peak at 69.6 Hz had decreased. The weak peak at 89.5 Hz
had increased and several very weak peaks also appeared throughout the spectrum (Fig. 4c
and Fig. 5b). During further heating, both the position and the intensity of the triplet
remained nearly constant. After 12 hours of heating, the peaks at 73.4 Hz and 93.5 Hz
gradually moved upfield as the former peak decreased in size; the latter peak remained
nearly constant (Fig. 4). Because the spectra were relatively simple compared to those
of H_4EDTA, the solution was not heated longer than 28 hours to allow sufficient sample
for later analysis of the products in the sealed tube.

The strong peak which shifted upfield from 71.8 Hz initially to 96.0 Hz after 28 hours
at 200°C is attributed to the methylene protons of H_3NTA in solution. Consequently, the
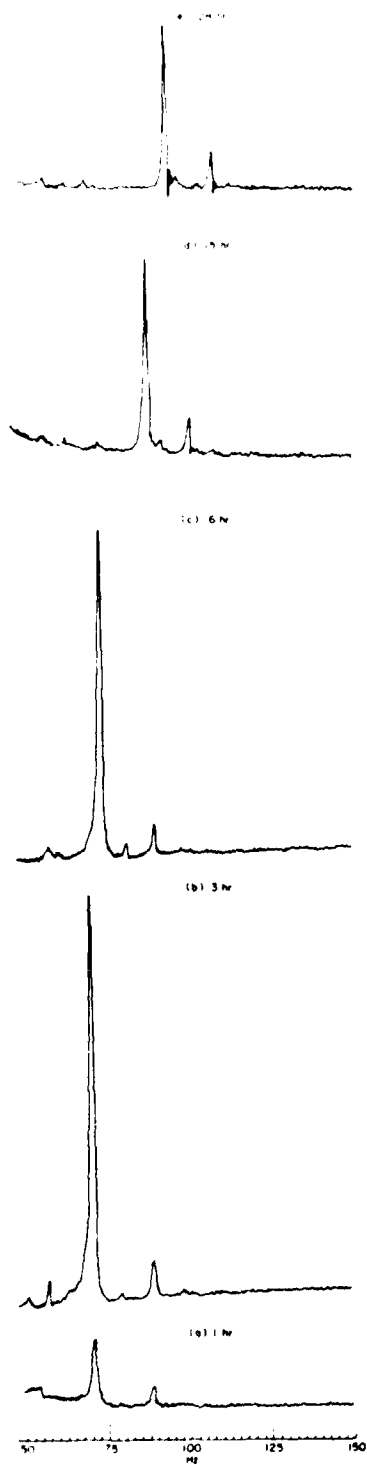
Fig. 4 - Nmr spectra of a 0.3M solu-
tion of H_3NTA sealed under reduced
pressure and heated to 200°C (50 to
150 Hz region)

rate of decomposition of the acid can be followed by the decrease in the intensity of the strong peak. Because the spectra were measured under identical conditions, the decrease in height of the peak initially at 71.8 Hz should be a measure of the rate of disapperance of H_3NTA. The data obtained in this way gives nonlinear zero-order and first-order rate plots; however, a linear plot is obtained if second-order kinetics is assumed (Fig. 6). Figure 6 shows that two different rates, or combination of rates, occur. The initial rate of decomposition is faster than the rate after 12 hours of heating when the heights of the triplet peaks reach a maximum and then start to decrease. Based on the faster rate and on the initial concentration employed, one-half of the H_3NTA has decomposed after 12 hours at 200°C. This compares with the reported (2) 13 hours for one-half of a Li_4EDTA solution (0.1M) to decompose at 200°C.

Fig. 5 - Nmr spectra of a 0.3M solution of H_3NTA sealed under reduced pressure and heated to 200 °C (150 to 250 Hz region)
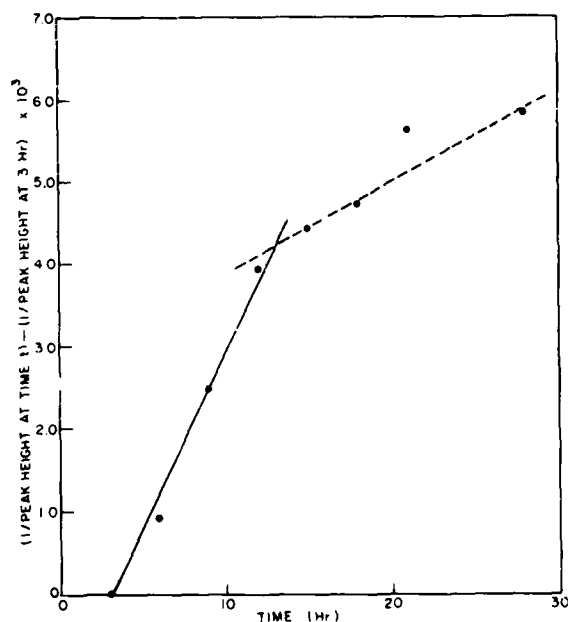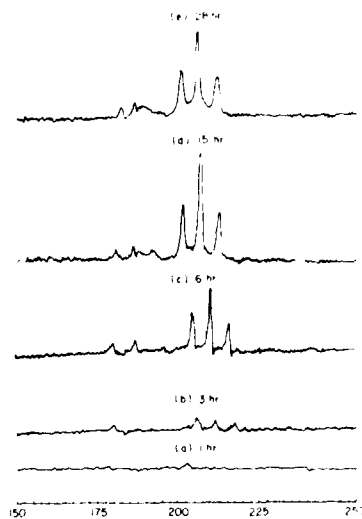

Fig. 6 - Second-order rate plot for the decomposition of 0.3M H_3NTA solution at 200°C

CONCLUSIONS

The estimated half-lives at 200°C of the chelating agents tested so far by the nmr technique are summarized in Table 1. Under the conditions of the experiments, solutions of the sodium salts of NTA   are far more stable than solutions of sodium or lithium $EDTA^{4-}$. Even H_3NTA appears to show a remarkable stability in aqueous solution at 200°C compared to H_4EDTA.

The observed enhanced thermal stability of H_3NTA, Na_2HNTA, and Na_3NTA compared to H_4EDTA, Na_2H_2EDTA, and Li_4EDTA is consistent with the proposal that the thermal decomposition of $EDTA^{4-}$ proceeds through a three-center hydrogen bridge. NTA^{3-}, unable to form a similar three-centered bridge, is relatively more stable up to 200°C, the temperature limit in this investigation. For the acid, H_3NTA, which dissolves only after several hours of heating, the decomposition rate is approximately the same as that of Li_4EDTA solutions, the most stable of the $EDTA^{4-}$ solutions studied (2). The apparent second-order kinetics, again similar to the Li_4EDTA solutions, suggests that in those solutions where the acid finally dissolves, a strong hydrogen bonding between the acid molecules, probably through the amine nitrogen, may provide the necessary intermediate structure for the stepwise decomposition of H_3NTA. Thus, the decomposition rate of NTA^{3-}, like $EDTA^{4-}$, occurs most rapidly in acid solutions (pH = 2), but where the hydrogen concentration is low, pH   8, the rate is extremely slow. The upfield movement of the ethylene proton peak in H_3NTA solutions is attributed to the removal of acidic protons by the ensuing thermal decomposition. The direction of peak shift is consistent with results reported by Chan, Kula, and Sawyer (5). The observed reduced rate of thermal decomposition after 20 hours of heating (Fig. 6) may be the result of a substantially increased pH.

Trace quantities of oxygen do not appreciably affect the rate of the thermal decomposition of NTA^{3-}. However, a study of the effect of dissolved oxygen on the rate of decomposition of Na_4EDTA in air-saturated, degassed and undegassed solutions shows a marked effect on the rate of decomposition (6).

Although the laboratory results show that NTA^{3-} is far more stable than $EDTA^{4-}$ at 200 C, it would be unsafe to predict that NTA^{3-} would continue to show excellent thermal stability at significantly higher temperatures (e.g., the 300° to 320°C temperatures of high-pressure boilers). A different mode of thermal decomposition, not dependent on protonation of NTA^{3-}, may control the rate at such temperatures; consequently, further testing of NTA^{3-} solutions is necessary at higher temperatures than the present 200°C limit imposed by the technique used in this work. However, our results indicate that contamination from thermally decomposed NTA^{3-} in basic solutions should be minimal and should occur only after prolonged heating at 200°C.

REFERENCES

1. Venezky, D.L., "Thermal Stability of Ethylenedinitrilotetraacetic Acid and Its Salts, Part 1 - A Literature Survey," NRL Report 6674, Dec. 1967

2. Venezky, D.L., and Moniz, W.B., Anal. Chem. 41:11 (1969)

3. Fujiwara, Y., and Reilley, C.N., Anal. Chem. 40:890 (1968)

4. Venezky, D.L., and Moniz, W.B., NRL Report in preparation

5. Chan, S.I., Kula, R.J., and Sawyer, D.T., J. Am. Chem. Soc. 86:377 (1964)

6. Venezky, D.L., NRL Report in preparation

DOCUMENT CONTROL DATA - R & D

Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Naval Research Laboratory	Unclassified
Washington, D.C. 20390	2b. GROUP

3. REPORT TITLE

THE THERMAL STABILITY OF NITRILOTRIACETIC ACID AND ITS SALTS IN AQUEOUS SOLUTIONS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

An interim report; work on the problem is continuing.

5. AUTHOR(S) (First name, middle initial, last name)

D.L. Venezky and W.B. Moniz

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
November 17, 1970	11	6
8a. CONTRACT OR GRANT NO	9a. ORIGINATOR'S REPORT NUMBER(S)	
NRL Problems C05-29 and C07-04		
b. PROJECT NO	NRL Report 7192	
RR 007-02-41-5678		
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
RR 001-05-42-4806		
d.		

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Department of the Navy (Office of Naval Research), Arlington, Va. 22217

13. ABSTRACT

A proposed mechanism for the thermal decomposition of ethylenedinitrilo-tetraacetic acid (H_4EDTA) and its salts suggests an intermediate having a hydrogen three-centered bridge structure. To elucidate the mechanism of $EDTA^{4-}$ decomposition and to establish structures which would impart inherent thermal stability to a chelating compound, nuclear magnetic resonance (nmr) techniques were used to study the thermal stability of nitrilotriacetic acid (H_3NTA) and its salts. These compounds have a structure similar to $EDTA^{4-}$ but are not capable of forming a three-center intramolecular bridge under any circumstance.

Degassed and undegassed aqueous solutions of Na_3NTA and Na_2HNTA and a degassed solution of H_3NTA were heated at 200°C in sealed nmr tubes for periods ranging from 1 hr to over 670 hr. Periodic examination of the contents using proton magnetic resonance (pmr) showed that dissolved oxygen has little effect on the decomposition of Na_3NTA and Na_2HNTA solutions. For one-half of the initial concentrations to decompose at 200°C, the estimated times for both degassed and undegassed solutions of Na_3NTA and Na_2HNTA were greater than 1000 hr. The estimated $t_{1/2}$ for H_3NTA solutions is 12 hr, for H_4EDTA solutions, 1 hr, and for Li_4EDTA solutions, the most stable $EDTA^{4-}$ solutions studied so far by the nmr techniques, 13 hr. Although the laboratory results show that NTA^{3-} is far more stable than $EDTA^{4-}$ at 200°C, it would be unsafe to predict that NTA^{3-} would continue to show this excellent thermal stability up to 300 through 320°C. A different mode of thermal decomposition, not dependent on the proposed protonation of NTA^{3-}, may

DD ,FORM,.**1473** (PAGE 1)

S/N 0101-807-6801

9

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Boiler corrosion Ethylenedinitrilotetraacetic acid (EDTA) Nitrilotriacetic acid (NTA) Nuclear Magnetic resonance technique Organic chelating agents Corrosion inhibition Boiler-water treatment Thermal stability of chelates						

occur readily at temperatures higher than 200°C. In basic solutions at 200°C and lower, the uncomplexed or weakly complexed NTA^{3-} should be stable enough to be useful as a boiler-water additive for sludge control and feed-water conditioning. Under the restrictive conditions, water contamination from thermally decomposed NTA^{3-} should be minimal and should occur only after prolonged heating.